ELECTRICAL ENGINEERING RESEARCH LABORATORY
ENGINEERING EXPERIMENT STATION
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

STATUS REPORT
ON
RESEARCH ON THE ELECTRICAL PROPERTIES
OF
SEMI-CONDUCTORS

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to

30 January 1954

Approved by:
T. A. Murrell

T. A. Murrell
Associate Professor

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1. INTRODUCTION

1.1 Purpose

This is the sixth status report on the lead telluride investigation being carried out under ONR sponsorship at the University of Illinois. This report covers the period 1 December 1953 to 28 February 1954. The purpose of the investigation is to study the semi-conducting properties of PbTe single crystals of various compositions.

1.2 Personnel

A considerable cut in funds has necessitated a readjustment of personnel.

The half-time appointments of Mr. Sirrine and Mr. Golubjatnikov are continuing. Mr. Pfluger, who works on an hourly basis, has averaged some 10 hours per week on the project. Professor Murrell has shifted to full-time teaching for the semester commencing in February, and has considerably less time available to the research program than formerly.

1.3 Summary

During the period covered by this report, several single crystals were produced, but none exhibited resistivities higher than 5×10^{-3} ohm-cm for p-type or 2×10^{-2} ohm-cm for n-type regions. All likely sources of uncontrolled impurities have been examined, one by one. The most important effort was directed toward rigorous purification of the lead and tellurium constituents. It is now believed that all significant impurity sources are eliminated, or will be shortly. The next approach toward achieving high resistivity material will be heat treatment under controlled pressures of tellurium vapor.

2. EQUIPMENT AND FACILITIES

2.1 Variable Dropping Rate Control

The dropping rate of the sample through the Stockbarger-Bridgman furnace is controlled by an electric clock motor and a system of reduction gears and pulleys. Previously the rate was changed by substitution of clock motors or pulley trains. Mr. Golubjatnikov has designed an oscillator-controlled power source for the motor, which provides successful operation from 25 to 240 cycles.

2.2 Lead Purification System

Mr. Sirrine has designed and constructed a distillation system that has been used to further purify the lead. As received from the supplier, the lead is better than 99.999% pure. The still consists essentially of a cold finger, cooled by water; a surrounding tube through which hydrogen can be passed, or which can be evacuated; and a removable bottom section. Two bottom sections are used, one, a flask containing the lead to be purified, surrounded by a furnace, and the other, a somewhat deeper flask surrounded by liquid nitrogen, and used to collect the distilled lead. In operation, the tube surrounding the finger is flushed several times with hydrogen, and then pumped down to about 5×10^{-6} mm of Hg. The cooling water and furnace are turned on, and about two-thirds of the charge is vaporized and condensed onto the cold finger. The liquid nitrogen cooled collecting flask is then substituted, and the purified lead melted off the finger under an atmosphere of hydrogen. The entire apparatus is constructed of vycor. Dr. Harry Letaw's advice and suggestions are gratefully acknowledged.

3. SUMMARY OF ACTIVITIES

3.1 Dropping Rate

To date all the crystals grown have been p-type at the bottom, the end which solidifies first, and n-type at the top, usually only the top few millimeters. The starting constituents have been weighed out to contain 50.2 or 50.3 atomic percent of lead. There is invariably a cap of free lead found at the top of the crystal. The obvious conclusion is that excess lead is excluded during the growth process, and that as solidification progresses, the increasing amount of excess lead finally produces n-type material. It has been found that higher dropping rates cause the p-n boundary to occur farther down the crystal. During this report period, one single crystal was produced at a dropping rate of 32 mm/hr, as compared with the usual rate of 3 to 5 mm/hr. In this case the upper third of the crystal was n-type, and the rest p-type.

3.2 Possible Sources of Impurities

The highest resistivity that has been produced so far is 5×10^{-3} ohm-cm for p-type material, and 2×10^{-2} ohm-cm for n-type, both measured at room temperature. Furthermore, in a given crystal, the resistivity does not vary as much as a factor of ten within a p-type region of several centimeters in length. A number of possible sources of unknown impurities have been considered, and most of them have been eliminated.

3.2.1 Impurities in Lead Constituent

The lead as received is better than 99.999% pure. However, it was decided to set up a purification process, the main features of which are described above in Section 2.2. One crystal has been grown with the purified lead, with no change in resistivity. A small supply of exceedingly pure lead has been donated to us by a colleague, Dr. Slifkin, and will be tried in the near future. However, impurities in the lead appear to be ruled out.

3.2.2 Impurities in Tellurium Constituent

The purification procedure for tellurium, described in an earlier report, has been to carry out fractional distillation twice. A spectroscopic analysis of one sample showed a trace of lead to be the only

observable impurity. Nevertheless, a more rigorous process is now being undertaken, whereby the number of repeated distillations will be increased to five or six.

3.2.3 Oxygen Impurities

It is well known that the presence of oxygen in the growing apparatus will produce a low resistivity p-type material. This possibility has been eliminated by extended heating of the constituents, especially the lead, in a stream of hydrogen prior to mixing, and sealing of the quartz crucible under a partial pressure of hydrogen. Confirmation has been added by the fact that no significant difference resulted from the use of a pure carbon boat.

3.2.4 Hydrogen Compounds

A somewhat unlikely possibility is that hydrogen compounds may remain in the constituents and act as acceptor impurities. Provisions are being made to sweep out the hydrogen with either argon or helium of high purity just before final mixing takes place.

3.2.5 Reactions with Quartz

Several crystals have been grown in a pure carbon boat lining the quartz crucible. No appreciable difference in resistivity was found, and it is believed that reaction with the quartz can be ruled out.

3.2.6 General Cleanliness

All pyrex, vycor, and quartz ware used in the mixing and growing process has been thoroughly cleaned for each run, and then outgassed before use. As a final precaution, the last two runs included boiling the apparatus several times in triple-distilled water.

3.3 Conclusions

With the completion of the steps now under way, the possibility of unknown impurities would seem to be effectively eliminated. The conclusion would then present itself that the phase relations between Pb, Te and PbTe in the liquid and in the solid state are such that a crystal of stoichiometrically pure PbTe cannot be grown by the Stockbarger-Bridgman method, and that the dynamics of growth result in low resistivity material on both sides of the p-n boundary. If this is correct,

then two different approaches might result in higher resistivity material. The first would be to grow small crystals from a large melt by a crystal pulling method. The second, and certainly the simpler, would be to attempt to bring an entire sample closer to the correct stoichiometric composition by diffusion at elevated temperatures in a controlled pressure of tellurium vapor. By adjusting the pressure and the length of diffusing time, it should also be possible to produce p-n junctions.

4. PLANS FOR THE NEXT INTERVAL

During the next interval, the remaining steps indicated above for the rigorous purification of the constituents will be completed. If the results turn out to be negative, as seems likely diffusion in controlled tellurium vapor pressure will be investigated.